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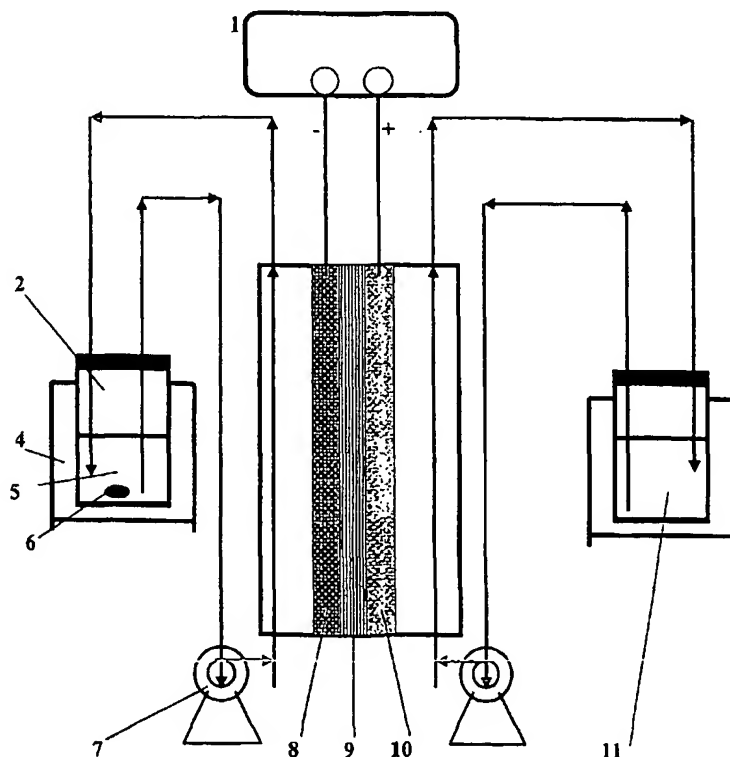
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(54) Title: **ELECTROLYSIS CELL AND METHOD**



(57) Abstract: A zero-gap solid polymer electrolyte electrolysis cell is provided comprising an anode; a cathode; and an ion exchange membrane disposed between the anode and the cathode; wherein the cathode is a catalyst comprising a hydrogen sorbing material. This cell can be used in the dehalogenation of halogenated organic compounds and the destruction of aqueous nitrates.

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ELECTROLYSIS CELL AND METHOD

The present invention relates to an electrolysis cell and a method of using that cell in the dehalogenation of halogenated organic compounds, and in the reduction of nitrates.

Halogenated organic compounds are toxic to biological systems and, almost invariably, resistant to bio-degradation by the micro-organisms commonly employed in bio-remediation plants.

10 The annual tonnage of halogenated organic waste in the UK in 1995-1996 was approximately 1 million tonnes. Disposal of this waste in landfill sites is now virtually completely prohibited by the Environment Agency, and disposing of this waste by incineration has high costs, as well as presenting a

15 risk due to harmful by-products. Although the relevant industries have put in place recovery procedures for the reuse of halogenated organic, there is still a substantial amount of waste material to be handled.

20 Chemical and electrochemical methods have been suggested for the treatment of these compounds, but suffer from a number of problems. Chemical methods tend to be batch processes with their attendant disadvantages, including high handling costs, increased exposure to the toxic halogenated organics and

25 difficulties in maintaining maximum efficiency over varying batches. Some electrochemical methods that have been suggested have also been batch processes, and therefore have the same disadvantages as chemical methods. Other methods that have been suggested have required the use of an aqueous

30 catholyte, which entails problems in dissolving the organic compounds. Even if it is possible to derive such a catholyte, the increased cost of this pre-treatment makes such treatment methods less economical.

Nitrate, NO_3^- , is a widespread contaminant of ground and surface water; the US EPA Office of Water document "Is your water safe" (EPA 570 9-91-005, Sep. 1991) states that

5 "...only two substances for which standards have been set pose an immediate threat to health whenever they are exceeded: bacteria and nitrate". The human health threat from nitrate arises from the fact that nitrate is converted to nitrite, NO_2^- , by bacteria in the gut, which then combines with

10 haemoglobin to form methemoglobin, reducing the oxygen-carrying capacity of the blood. Methemoglobinemia in infants is referred to as 'Blue Baby Syndrome'; in addition, chronic consumption of high levels of nitrate may cause other health problems such as some cancers and teratogenic effects. In

15 recent years, high nitrate discharges have been linked to instances of inland and coastal waters eutrophication, due to algal blooms, and is now recognised as a global problem linked to the intensive use of fertilisers. Adequate methods of reducing nitrate contamination in water which combine

20 efficiency with economy are not available.

The present inventors have now developed an electrolysis cell which eliminates the need for aqueous catholyte and allows for continuous processing, as well as methods of at least

25 partially dehalogenating halogenated organic compounds. The invention also finds use in treating aqueous systems, and in batch operation. The invention can also be used in treating aqueous nitrate systems, to reduce nitrate contamination.

Accordingly, the first aspect of the invention provides a zero-gap solid polymer electrolyte electrolysis cell comprising

- (a) an anode;
- 5 (b) a cathode;
- (c) an ion exchange membrane disposed between the anode and the cathode;

wherein the cathode is a catalyst comprising a hydrogen sorbing material.

10

Zero-gap solid polymer electrolyte cells are characterised by the anode and the cathode being immediately adjacent the ion exchange membrane, which serves as the solid polymer electrolyte.

15

Further features and preferences of the first aspect will now be described.

Cathode

- 20 The catalyst must comprise a hydrogen sorbing material, and preferably consists of a hydrogen sorbing material, or a mixture of hydrogen sorbing materials. These hydrogen sorbing materials are selected from: palladium, nickel, iron, chromium and the lanthanides. The hydrogen sorbing material is
- 25 preferably selected from palladium, nickel, and iron, and more preferably is palladium.

- The catalyst may be supported on a substrate, which substrate may also act as a current collector. If the catalyst is not
- 30 supported or is only supported on a substrate with no large scale structure, e.g. a powder, it may be deposited directly onto the ion exchange membrane. A current collector is then pressed against such a catalyst or its substrate.

Current collector

The current collector may be metallic or made from carbon. Options for the structures of a metallic collector include
5 mesh, foam and fibre.

Suitable metal meshes vary in aperture size from 149 μ m to 2380 μ m (800 to 8 mesh), with the larger aperture meshes being called 'expanded metals' and the smaller aperture sizes being
10 called 'mini-meshes'.

Metal foams are a three-dimensional structures with aperture sizes of about 2 μ m to 500 μ m. They may vary in thickness from 50 μ m up to 1000 μ m or more.

15

A metal fibre collector is a woven cloth, where the individual threads are metal. Typically the fibres have a diameter of between 1 and 10 μ m, and the cloth has a porosity of typically between 80 and 95%.

20

Suitable metals for the collector include titanium, tantalum, nickel, steel, iron and alloys of these metals.

Options for the carbon structure include cloth, felt, paper,
25 foam and fibre, with similar physical properties to their metal counterparts.

Preferred cathode structures are catalysts supported on titanium mini-mesh, iron gauze or carbon cloth.

30

Ion exchange membrane

The ion exchange membrane can be any suitable material which allows the passage of at least one ion involved in the electrolytic processes at the anode and the cathode.

5

The membrane may be classified according to the type of ion transported, i.e.:

- a) cation transfer - selective to the transport of positively charge ions, such as H^+ ;
- 10 b) anion transfer - selective to the transport of negatively charged ions, such as OH^- , Cl^- ;
- c) bipolar - can split water into H^+ and OH^- by application of a potential difference across membrane.

- 15 The membrane can also be classified by its material, i.e. inorganic, organic or inorganic/organic composite.

Examples of organic membranes include, but are not limited to, those based on fluorocarbon, hydrocarbon or aromatic polymers
20 with or without side chains, e.g. divinyl benzene with active exchange groups, such as sulphonate and carboxylate for cation exchange, and amine for anion exchange.

Particularly preferred organic membranes include Nafion, a
25 fluorosulphonate ionmer, more particularly a perfluorosulphonic acid PTFE copolymer, and Fumatech FT-fKE-S, which has amine based exchange groups.

Examples of inorganic membranes include, but are not limited
30 to, nano-porous membranes with an immobilised acid, e.g. SiO_2 /PVDF binder/sulphuric acid.

Examples of organic/inorganic composite membranes include Nafion/phosphate, Nafion/silica and Nafion/ZrO₂.

Anode

- 5 The anode can be any suitable electronically conducting material to ensure a counter electrode reaction to that occurring at the cathode. This counter electrode reaction may include oxygen evolution, hydrogen oxidation, organic oxidation, oxidation of inorganic species. Its structure can
10 be similar to that of the cathode, but also can bear a different catalyst, as appropriate.

The anode may be selected so as to be able to oxidatively destroy the product of the reaction at the cathode, such that
15 the cell is connected so that the products from the reaction at the cathode are fed to the anode.

SnO₂, Pt, RuO₂, PbO₂, IrO₂, Ni, Ti₄O₇ and TiO₂ electrodes and Dimensionally Stable Anodes (DSAs) are suitable for such
20 oxidation reactions.

A second aspect of the invention provides a method of at least partially dehalogenating a halogenated organic compound using a solid polymer electrolyte cell of the first aspect,
25 including the steps of simultaneously:

- (a) passing a liquid comprising a halogenated organic compound over the cathode of the cell;
- (b) passing a suitable anolyte over the anode of the cell;
- and
- 30 (c) applying a voltage across the cathode and anode.

The catholyte may be aqueous or non-aqueous, or a mixture of both as a dispersion, and usually comprises the halogenated

organic compound in solution, although neat halogenated organic compounds can be the catholyte, mixed with or dispersed in an oil.

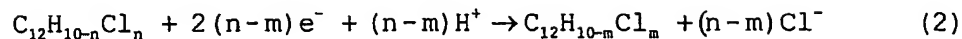
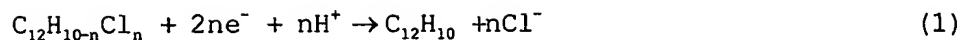
- 5 The anolyte can be aqueous or non-aqueous and capable, or not, of passing ions.

The anode of the cell can be capable of further treating the products from the reaction at the cathode, and the method
10 includes the step of the result of the process at the cathode being passed to the anode as the anolyte. This process can occur either by directing the exit flow from the cathode part of the cell to the in flow of the anode part of the cell, or by the treated catholyte passing through the membrane to the
15 anode part of the cell. This can be achieved by diffusion, electro-osmosis and/or convection of fluid under, for example, a pressure gradient.

Halogenated organic compounds

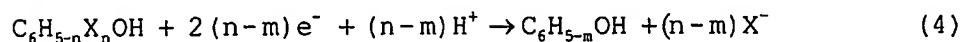
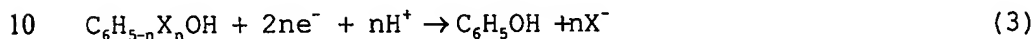
- 20 The method of the second aspect of the invention is suitable for at least partially dehalogenating any halogenated organic compound, i.e. an organic molecule bearing at least one halogen substituent. In one embodiment, the halogenated organic compounds are those bearing halogen substituents on
25 aromatic rings, and in particular, carboaromatic rings, i.e. aromatic rings consisting of carbon atoms linked by chemical bonds in a ring.

For example, polychlorobiphenyl compounds of the formula
30 $C_{12}H_{10-n}Cl_n$, can be reduced to the biphenyl compound, either bearing no chloro substituents (1) or bearing less chloro substituents (2):



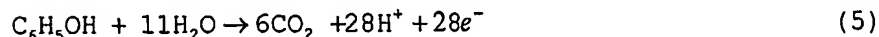
where n and m are integers, and m is less than n.

5 A further example, is the reduction of halophenol compounds of formula $\text{C}_6\text{H}_{5-n}\text{X}_n\text{OH}$, where X is a halo substituent (e.g. Br, Cl), to either phenol (3) or a halophenol bearing less halo substituents (4):



where n and m are integers, and m is less than n.

The oxidation of phenol at a suitable anode can be represented
15 as follows (5):



A third aspect of the invention provides a method of at least
20 partially reducing aqueous nitrate ions using a solid polymer electrolyte cell of the first aspect, including the steps of simultaneously:

- (a) passing an aqueous solution of nitrate ions over the cathode of the cell;
- 25 (b) passing a suitable anolyte over the anode of the cell;
- and
- (c) applying a voltage across the cathode and anode.

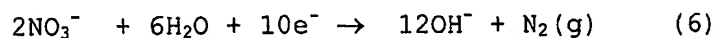
The anolyte can be aqueous or non-aqueous and capable, or not,
30 of passing ions.

The anode of the cell can be capable of further treating the products from the reaction at the cathode, and the method includes the step of the result of the process at the cathode being passed to the anode as the anolyte. This process can
5 occur either by directing the exit flow from the cathode part of the cell to the in flow of the anode part of the cell, or by the treated catholyte passing through the membrane to the anode part of the cell. This can be achieved by diffusion, electro-osmosis and/or convection of fluid under, for example,
10 a pressure gradient.

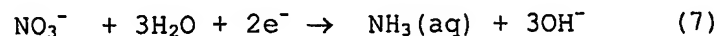
Nitrate ions

The method of the third aspect of the invention is suitable for at least partially reducing an aqueous solution of nitrate
15 ions. These nitrate ions may be present in the water by a number of different, and well documented, processes.

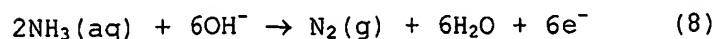
The reduction is likely to proceed by one of two possible routes depending on the reaction conditions employed. The
20 first route reduces an aqueous solution of nitrate ions to nitrogen gas, as follows (6):



25 An alternative route would result in the reduction of an aqueous solution of nitrate ions to ammonia, as follows (7):



30 This could be coupled to a reaction at the anode, where the ammonia is oxidised to nitrogen, as follows (8):



In both of the above reactions, the membrane employed in the cell could be an anion exchange membrane.

The present invention will now be described by way of example,
5 with reference to the drawings in which:

Fig. 1 shows a cell and rig according to the invention;

Fig. 2a shows the amount of chloride ions released over time
10 from dichlorophenol (DCP) in cells of the invention, with a palladised carbon cloth cathode (A) and a palladised activated carbon powder cathode (B);

Fig. 2b shows the same as Fig. 2a but when the catholyte
15 contains pentachloro-phenol (PCP);

Fig. 3 shows the variation in the rate of chloride ion released from DCP on varying the palladium loading on the carbon powder cathodes;
20

Fig. 4 shows the variation in the rate of chloride ion released from DCP on varying the temperature at which the cell operates;

25 Fig. 5 shows the amount of chloride ions released over time from DCP (A) and PCP (B) in a cell of the invention having a palladised titanium mesh cathode;

Fig. 6 shows the variation in the rate of chloride ions released from DCP on varying the palladium loading on titanium
30 mesh cathodes;

Fig. 7 shows the variation in the rate of chloride ion released from DCP on varying the nature of the catholyte in cells of the invention;

5 Fig. 8 shows the variation in concentration of starting materials (DCP) and products in one of the cells of Figure 7; and

10 Fig. 9 shows the destruction percentage of dichlorophenol and dibromophenol in paraffin oil in a cell of the present invention.

Examples

15 Construction of Solid Polymer Electrolyte (SPE) Zero Gap Cell

Membranes

Two membranes were used in the SPE cell, Nafion 117 (DuPont)
20 and FuMATech FT-FKE-S (FuMATech).

Pre-treatment of the Nafion 117 membranes was carried out using the following procedure. First, the membranes were heated at 80°C in 5% H₂O₂ solution for 1 hour to remove any
25 residual organic species present. The membranes were thoroughly washed with Millipore conductivity water and boiled in 1 M aqueous sulphuric acid for 2 hours. Following washing, the electrodes were then boiled in Millipore conductivity water for a further 1 hour to introduce a reproducible amount
30 of water into each sample. The membrane was then washed with Millipore conductivity water several times to remove the protons that were not tightly bound or exchanged on the membranes. The pre-treated membranes were finally kept in Millipore conductivity water.

The FuMATech FT-FKE-S membranes (FuMATech) were used after immersion in water for 2 hours.

5 *Cathodes*

Palladised Carbon cloth (0.5 to 10 mg Pd/cm²; 9 cm²)

Electrodeposition techniques, which ensure that catalyst material is not deposited at electrically and ionically isolated positions within the electrode, were used to prepare
10 palladised carbon cloth. The carbon cloth (GC-14, E-Tek Inc.) was degreased with acetone, washed with water, and the deposition carried out without drying. Two methods, constant potential (-200 to -1000 mV vs RHE) or constant current (5 -
50 mA cm⁻²), were used in the deposition process, with a
15 typical concentration of PdCl₂ of 1M. After palladisation, the palladised cathodes were washed with Millipore water at least five times to remove any possible chloride ion on the surface and used without drying. The palladium deposits obtained by
the above procedure were dark in colour. The deposits appeared
20 uniform to the eye, and were shown to be uniform by SEM and EDAX analysis. Electrical contact to the carbon cloth electrode was made through a Ti mesh or stainless steel mesh. Sealing of the cell was facilitated by wrapping the edges of these meshes with Teflon tape.

25

Palladised carbon powders (0.5 to 20 mg Pd cm⁻²)

Palladium-charcoal (5% or 10% Pd, BDH) and palladium-activated carbon powder (30% Pd, Aldrich) were used as received. The cathode consisted of a backing layer, a gas diffusion layer,
30 and a reaction layer. A teflonised carbon cloth (E-TEK, type A) of 0.35 mm thickness was employed as the backing layer. To prepare the gas diffusion layer, the required quantity of isopropanol was added to a pre-teflonised Ketjan black carbon

to make the paste required. The resulting paste was spread onto the carbon cloth and dried in an air oven at 70 to 95°C for 3 to 10 minutes. To prepare the reaction layer, the required quantity of Pd-C powder was mixed with 10 wt%
5 teflonised carbon. The required quantity of Nafion solution was added to the mixture with continuous stirring. The resulting paste was spread onto the gas diffusion layer of the electrode and dried in an air oven at 60 to 95°C for 3 to 15 minutes. Finally, a thin layer of Nafion was spread onto each
10 surface of the cathode. The cathode as part of a sandwiched MEA was connected to the power supply by stainless steel or graphite blocks.

Electrocatalyst on mesh

15 Electro-deposition techniques were used to prepare catalysed electrodes, i.e. Fe/Ti mesh, Ni/Ti mesh, Pd/Ti mesh, Pd-Ni/Ti mesh, and Pd-Ni/Stainless steel mesh, as follows. After degassing in acetone and washing in Millipore water, the substrates, e.g. Ti mesh (a 9cm² plain weaved mesh having an
20 open area of 37%, 0.38 mm nominal aperture size and 0.25 mm wire diameter) and stainless steel mesh (a 9cm² plain weaved/twill mesh having an open area of 38%, 0.19 mm nominal aperture size and 0.23 mm wire diameter), were pre-treated by chemical etching in 5 to 20 wt% oxalic acid or 5 to 27 wt% HCl
25 solution at 60 to 100°C for 1 to 15 minutes. The pre-treated substrates were mounted into an electrodeposition cell. The cell was then filled with N₂-saturated deposition solutions of known concentration, e.g. 0.1 M PdCl₂ solution, and stirred magnetically. The catalyst was electrodeposited onto the
30 substrate under potentiostatic control or at a constant current. The deposition potentials and/or current were chosen according to the appropriate linear voltammograms, ranging from 0 V to -1.0 V vs RHE and 5 to 25 mA cm⁻². The amount of

charge required to deposit the catalyst was monitored through a computer-controlled potentiostat (Model 273 EG&G Princeton). Following deposition, electrodes were extensively washed with boiling Millipore water.

5

Anode

Three types of anode were used, i.e. platinum mesh (open area 65%, nominal aperture 0.25 mm and wire diameter 0.06 mm, Goodfellow), catalysed anodes and gas diffusion anodes.

10

The catalysed anodes, e.g. Pt/carbon cloth, Pt/Ti mesh, RuO₂/carbon cloth and RuO₂/Ti mesh, were prepared using the methods described above.

15 The gas diffusion anodes, e.g. Pt/carbon powder and RuO₂/carbon powder, were prepared using the methods described above.

Assembly of cell

A sandwiched membrane electrode assembly (MEA) was obtained by
20 hot pressing the anode, e.g. platinum mesh (9 cm²), Pt/carbon cloth, Pt/Ti mesh, and the cathodes, e.g. Pd/Ti mesh, Pd/carbon cloth and Pd/carbon powder, on either side of the pre-treated membranes, i.e. Nafion 117 or FuMAtech FT-FKE-S, at 25 to 150 kg cm⁻² and 25 to 130°C for 3 to 20 minutes. The
25 thickness of the MEA was approximately 2 mm for the carbon powder cathodes and 1 mm for the mesh cathodes.

After allowing at least 24 hours to condition a new MEA in the test fuel cell at 20 to 60°C and atmospheric pressure with
30 continuous feed of 0.05 to 2.5 M H₂SO₄ solution, the MEA was used under the various operating conditions discussed below.

An SPE zero gap flow cell was assembled employing the above MEA sandwiched between two graphite or stainless steel blocks with machined flow channels. The ridges between the channels were responsible for the electrical contact with the backs of the electrode. The cell was held together using a set of retaining bolts positioned around the periphery of the cell.

The SPE zero gap flow cell was operated in a batch recirculation mode. The flow cell flow circuit, as shown in Figure 1, consisted of a laboratory scale two-electrode (cathode (8), anode (10)) cell with a membrane (9), two pumps (7) (H. R. Flow Inducer, England), reservoirs of anolyte (11) and catholyte (5), and thermostatic baths (4) (B-480 Waterbath, Buchi, Switzerland). In operation, catholyte and anolyte, each with a volume of 60 to 1000 ml, were pumped through the cell and then returned to the reservoirs for recycling by the pumps, which were calibrated before use. In some cases, the catholyte was stirred magnetically (6). The cell is shown as being attached to a power supply (1).

Preliminary runs were performed with flow rates between 50 and 500 cm³/min. All the electrolyses in the flow cell were carried out at constant current density, ranging from 5 to 100 mA cm⁻² or at a constant cathode potential of between -0.8 to -1.5 vs Reversible Hydrogen Electrode, for a period between 30 minutes and 20 hours. The concentrations of chloride, reactant, intermediates and products were monitored during the electrolysis using a chloride ion sensor and/or an HPLC.

Example 1: Carbon supported palladium cathodes

30

Two types of carbon supported palladium cathodes were used in the above described electrolysis cell, and comparisons made

between them. Figure 2a shows the concentration of released chloride ions over time for both the palladised carbon cloth (10 mg Pd/cm²) (A) and 30% palladium activated carbon cathode (15 mg Pd/cm²) (B) when the catholyte was a 10mM dichlorophenol (DCP) solution. Figure 2b shows the same figures when the catholyte was a 1mM solution of pentachlorophenol (PCP). For both cells, the other conditions were as follows:

Membrane	Nafion 117
Current collectors & electrolyte flow channels	Stainless steel blocks
Controlled current	300 mA
Anolyte	100 ml H ₂ O
Catholyte solvent	100 ml H ₂ O
Temperature	21.5 ± 0.5°C
Flow rate	150 ml/min

Changing the catalyst loading of the cathode increases the amount of chloride ions released over time, as shown in Figure 3, where the three different palladium on carbon powder cathodes were used to dechlorinate a 1mM DCP solution: 30% Pd/activated carbon powder (15 mg Pd/cm²) (A), 10% Pd/charcoal (5 mg Pd/cm²) (B), 5% Pd/charcoal (2.5 mg Pd/cm²) (C). The conditions were as above, but with a controlled current of 500 mA.

Effects of other variables on the dechlorination were investigated.

With the palladised carbon cloth cathode, dechlorination could be carried out with a current as low as 20 mA, although a current of about 50 mA produced the best results, with the amount of chloride produced falling at 300 mA. For the

palladised carbon powder cathodes, current above 100 mA produced good results, with the most effective current lying in the range of 300 to 600 mA.

- 5 Changing the membrane to the FuMATech membrane resulted in a lower amount of chloride ions released. Although increasing the concentration of the catholyte from 1mM to 20mM produced more chloride ions, the efficiency of the cell decreased. Increasing the temperature released more chloride ions and
- 10 promoted a higher efficiency, as shown in Figure 4. This illustrates the amount of released chloride ions against electrolysis time for a 10mM solution of DCP using the 30% Pd/activated carbon cathode under the following conditions:

Membrane	Nafion 117
Current collectors & electrolyte flow channels	Stainless steel blocks
Controlled current	300 mA
Anolyte	100 ml H ₂ O
Catholyte solvent	100 ml H ₂ O
Temperature	20.5°C (A) 35°C (B) 50°C (C) 70°C (D)
Flow rate	150 ml/min

15

Example 2: Palladium on Titanium Mesh Cathode

- A palladium on titanium mesh cathode as described above with a palladium loading of 10 mg/cm² was used in the above described
- 20 electrolysis cell. Figure 5 shows the concentration of released chloride ions over time when the catholyte was:
- (i) a 10mM dichlorophenol (DCP) solution (A); and

(ii) a 1mM pentachlorophenol (PCP) solution (B).

For both cells, the other conditions were as follows:

Membrane	Nafion 117
Current collectors & electrolyte flow channels	Stainless steel blocks
Controlled current	50 mA
Anolyte	100 ml H ₂ O
Catholyte solvent	100 ml H ₂ O
Temperature	22.0 ± 0.5°C
Flow rate	150 ml/min

- 5 Effects of other variables on the dechlorination of DCP were investigated in a similar way to example 1.

Dechlorination could be carried out with a current as low as 20 mA, with the best amount of chloride ions released at 300
10 mA. Increasing the concentration of the catholyte from 1mM to 10mM produced more chloride ions, the efficiency of the cell decreased. Increasing the temperature from 22°C to 70°C released more chloride ions and promoted a higher efficiency.

- 15 The effect of catalyst loading on this class of cathode was investigated by using palladised titanium meshes with loadings of 0.5 mg/cm² (A), 1.0 mg/cm² (B), 1.5 mg/cm² (C), 2.0 mg/cm² (D) and 5.0 mg/cm² (E) as shown in figure 6, where the cell was run under the following conditions:

Membrane	Nafion 117
Current collectors & electrolyte flow channels	Stainless steel blocks
Controlled current density	5 mA cm ⁻²
Anolyte	100 ml 0.05M H ₂ SO ₄
Catholyte	20 mM DCP in 100 ml 0.05M H ₂ SO ₄
Temperature	21.5 ± 0.5°C
Flow rate	150 ml/min.

The effect of changing the pH of the supporting electrolyte was investigated in a similar manner using a solution of 20 mM DCP under the following conditions, as shown in Figure 7

Membrane	Nafion 117
Cathode	Palladised Ti mesh (2 mg Pd cm ⁻²)
Current collectors & electrolyte flow channels	Stainless steel blocks
Controlled current density	5 mA cm ⁻²
Anolyte & Catholyte solvent	100 ml of: H ₂ O (A) 0.05M H ₂ SO ₄ (B) 0.05M Na ₂ SO ₄ (C) 0.05M NaOH (D)
Temperature	21.5 ± 0.5°C
Flow rate	150 ml/min.

Figure 8 shows the variation in the concentration of the starting material (DCP - A) and in possible products (Phenol - B; chlorophenol - C; chloride ion - D) under the above conditions, where the anolyte and catholyte solution were

0.05M H_2SO_4 , and where the cathode was a palladised Ti mesh with a palladium loading of 2 mg Pd cm^{-2} .

Example 3: Dechlorination of DCP/DBP in paraffin oil

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A palladised carbon cloth cathode (5 mg Pd cm^{-2}), along with a platinised carbon cloth anode (2 mg Pt cm^{-2}) were used in the above described electrolysis cell to dehalogenate DCP and dibromophenol (DBP) in a paraffin oil solution.

10

These carbon cloth anodes were prepared in a similar manner to the palladised carbon cloth anodes as described above, but the deposition step used a salt solution, e.g. 0.1 M PdCl_2 , and was followed by washing with Millipore water to remove any ions

15

which were not tightly bound to the cloth, and then the anodes were subject to chemical reduction. This chemical reduction was carried out using 50 ml of 0.1 M NaBH_4 solution for 10 to 100 minutes, after which the anode was soaked in Millipore water for 1 hour and then used without drying or dried

20

overnight in a vacuum oven at 80°C .

Figure 8 shows the amount of halogenated compounds destroyed over time. The cells were operated as follows:

Membrane	Nafion 117
Current collectors & electrolyte flow channels	Stainless steel blocks
Controlled current density	5 mA cm ⁻²
Catholyte	0.2M DCP(A) or DBP(B) in paraffin oil (white & light oil, with n(20°)=1.4680, density 0.838, F(p)>110°C)
Anolyte	0.5 M H ₂ SO ₄
Flow Rate	50 ml/min.
Temperature	19.2±0.3°C

Example 4: Dehalogenation of mixtures of halogenated phenols

- 5 A palladium on titanium mesh cathode as described above with a palladium loading of 10 mg/cm² was used in the above described electrolysis cell, along with a platinum mesh anode, to dehalogenate mixtures of halogenated phenols in aqueous solutions.

10

The cell was operated as follows:

Membrane	Nafion 117
Current collectors & electrolyte flow channels	Stainless steel blocks
Controlled current density	10 mA cm ⁻²
Catholyte	See below
Anolyte	0.05 M Na ₂ SO ₄ /H ₂ SO ₄
Flow Rate	50 ml/min.
Temperature	20.1±0.3°C

The following mixtures of halogenated phenols were used as the catholyte, in pH 3, 0.05M Na₂SO₄ solution. The destruction percentage at 3 hours for each halogenated phenol are given.

Isomer concentration	Destruction percentage (at 3hrs)
1mM 4-chlorophenol + 1mM 2,4-dichlorophenol	32.4 63.8
10mM 4-chlorophenol + 10mM 2,4-dichlorophenol	60.2 86.2
1mM 2-chlorophenol + 1mM 3,4-dichlorophenol + 1mM 2,4-dibromophenol	82.1 86.3 98.5
10mM 2-chlorophenol + 10mM 3,4-dichlorophenol + 10mM 2,4-dibromophenol	75.7 86.1 98.7

CLAIMS

1. A zero-gap solid polymer electrolyte electrolysis cell comprising
 - 5 a) an anode;
 - b) a cathode;
 - c) an ion exchange membrane disposed between the anode and the cathode;wherein the cathode is a catalyst comprising a hydrogen
10 sorbing material.
- 15 2. An electrolysis cell according to claim 1, wherein the hydrogen sorbing material is selected from palladium, nickel, iron, chromium and the lanthanides.
3. An electrolysis cell according to claim 2, wherein the hydrogen sorbing material is selected from palladium, nickel, and iron.
- 20 4. An electrolysis cell according to any one of claims 1 to 3, wherein the catalyst is supported on a substrate.
5. An electrolysis cell according to any one of claims 1 to 3, wherein the cathode further comprises a current collector.
25
6. An electrolysis according to any one claims 1 to 5, wherein the catalyst is supported on titanium mini-mesh, iron gauze or carbon cloth.
- 30 7. An electrolysis cell according to any one of claims 1 to 6, wherein the ion exchange membrane is an organic membrane.

8. An electrolysis cell according to any one of claims 1 to 7, wherein the ion exchange membrane is a fluorosulphonate ionmer.

5 9. An electrolysis cell according to any one of claims 1 to 8, wherein the anode is able to oxidatively destroy the product of the reaction at the cathode, such that the cell is connected so that the products from the reaction at the cathode are fed to the anode.

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10. An electrolysis cell according to claim 9, wherein the anode is selected from a SnO_2 , Pt, RuO_2 , PbO_2 , IrO_2 , Ni, Ti_4O_7 and TiO_2 electrode and a Dimensionally Stable Anode (DSA).

15 11. A method of at least partially dehalogenating a halogenated organic compound using an electrolysis cell according to any one of claims 1 to 8, including the steps of simultaneously:

- 20 (a) passing a liquid comprising a halogenated organic compound over the cathode of the cell;
- (b) passing a suitable anolyte over the anode of the cell; and
- (c) applying a voltage across the cathode and anode.

25 12. A method according to claim 11, wherein the catholyte comprises the halogenated organic compound in solution.

13. A method according to claim 11, wherein the catholyte comprises the halogenated organic compound mixed with or
30 dispersed in an oil.

14. A method of at least partially dehalogenating a halogenated organic compound using an electrolysis cell

according to either claim 9 or claim 10, including the steps of simultaneously:

- (a) passing a liquid comprising a halogenated organic compound over the cathode of the cell;
- 5 (b) passing a the result of the process at the cathode to the anode of the cell as the anolyte; and
- (c) applying a voltage across the cathode and anode.

15. A method according to claim 14, wherein the catholyte
10 comprises the halogenated organic compound in solution.

16. A method according to claim 14, wherein the catholyte
comprises the halogenated organic compound mixed with or
dispersed in an oil.

15

17. A method according to any one of claims 14 to 16, wherein
step (b) comprises directing the exit flow from the cathode
part of the cell to the in flow of the anode part of the cell.

20 18. A method according to any one of claims 14 to 16, wherein
step (b) comprises the treated catholyte passing through the
ion exchange membrane to the anode part of the cell.

19. A method according to any one of claims 11 to 18, wherein
25 the halogenated organic compound bears halogen substituents on
an aromatic ring.

20. A method according to claim 19, wherein the halogenated
organic compound is a polychlorobiphenyl compounds of the
30 formula $C_{12}H_{10-n}Cl_n$, wherein n is an integer.

21. A method according to claim 19, wherein the halogenated
organic compound is a halophenol compounds of formula

$C_6H_{5-n}X_nOH$, where X is a halo substituents and where n is an integer.

22. A method of at least partially reducing aqueous nitrate
5 ions using an electrolysis cell according to any one of claims
1 to 8, including the steps of simultaneously:

- (a) passing an aqueous solution of nitrate ions over the
cathode of the cell;
- (b) passing a suitable anolyte over the anode of the cell;
- 10 and
- (c) applying a voltage across the cathode and anode.

23. A method of at least partially reducing aqueous nitrate
ions using an electrolysis cell using an electrolysis cell
15 according to either claim 9 or claim 10, including the steps
of simultaneously:

- (a) passing an aqueous solution of nitrate ions over the
cathode of the cell;
- (b) passing a the result of the process at the cathode to the
20 anode of the cell as the anolyte; and
- (c) applying a voltage across the cathode and anode.

24. A method according to claim 23, wherein step (b)
comprises directing the exit flow from the cathode part of the
25 cell to the in flow of the anode part of the cell.

25. A method according to claim 23, wherein step (b)
comprises the treated catholyte passing through the ion
exchange membrane to the anode part of the cell.

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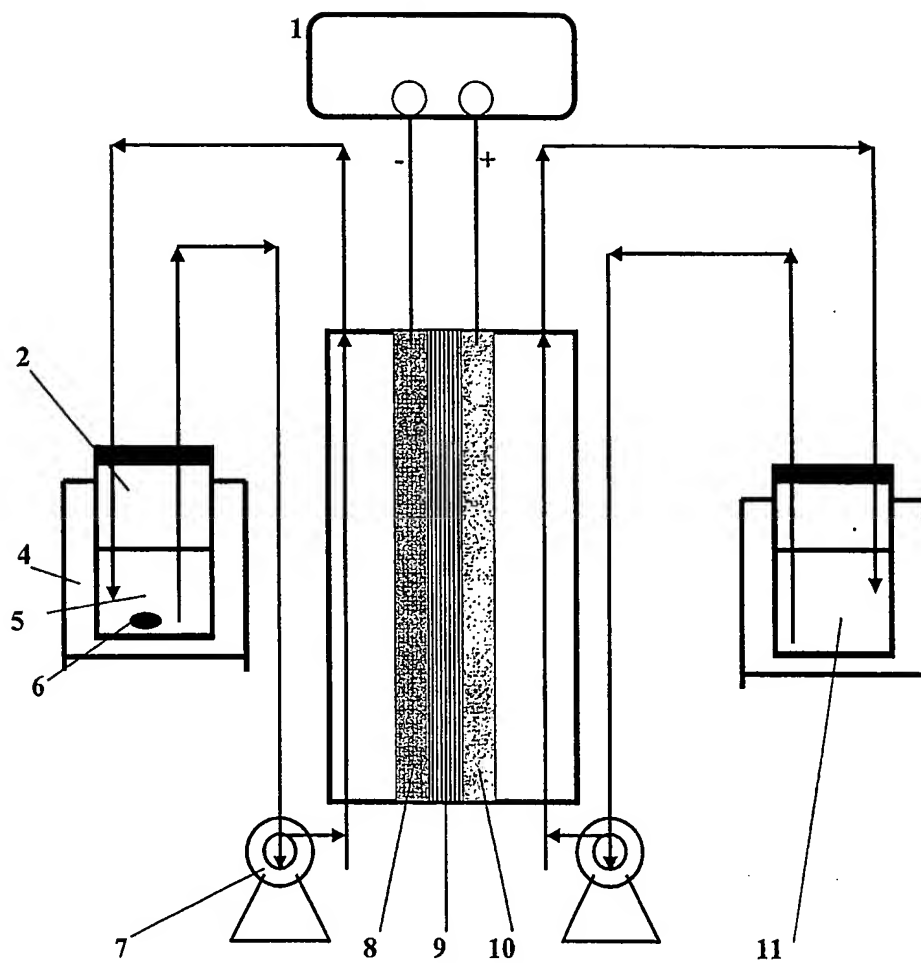


Figure 1

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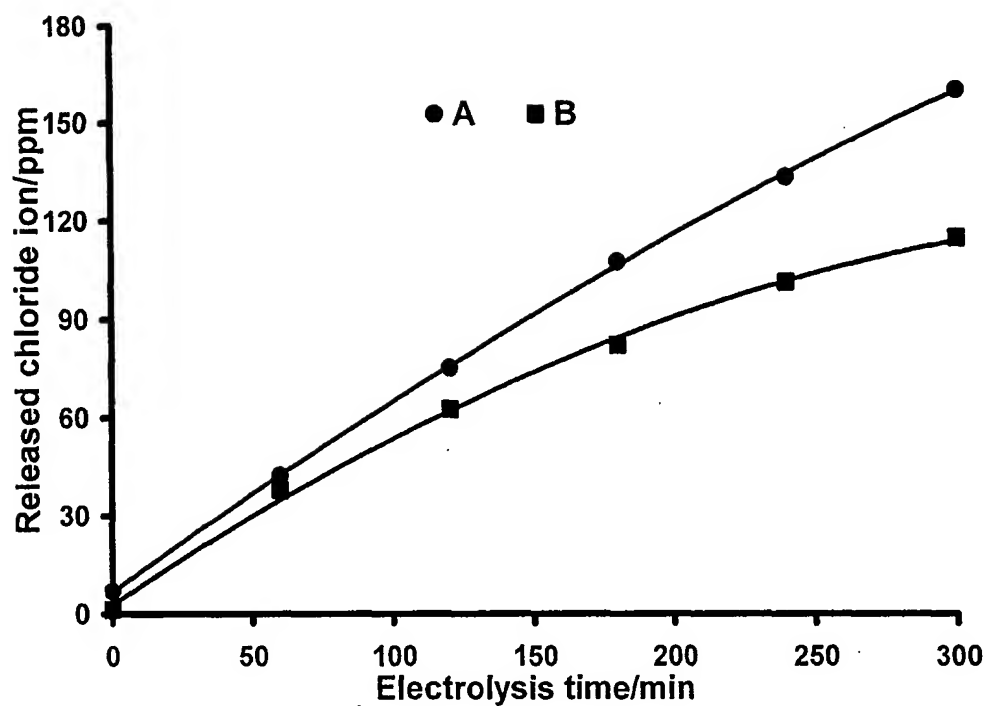


Figure 2a

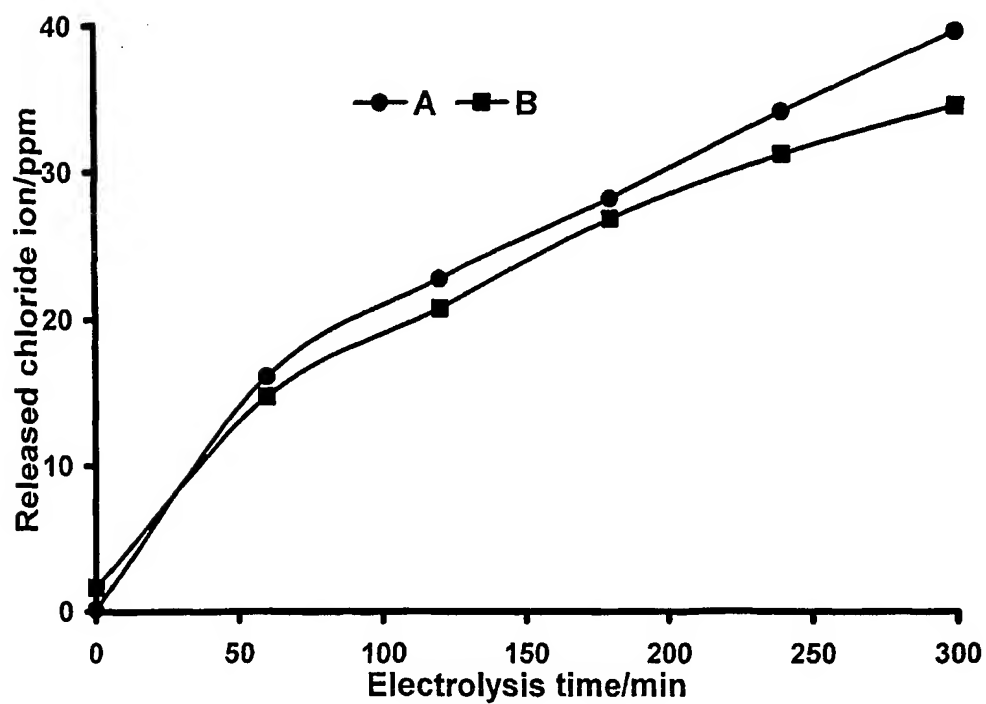


Figure 2b

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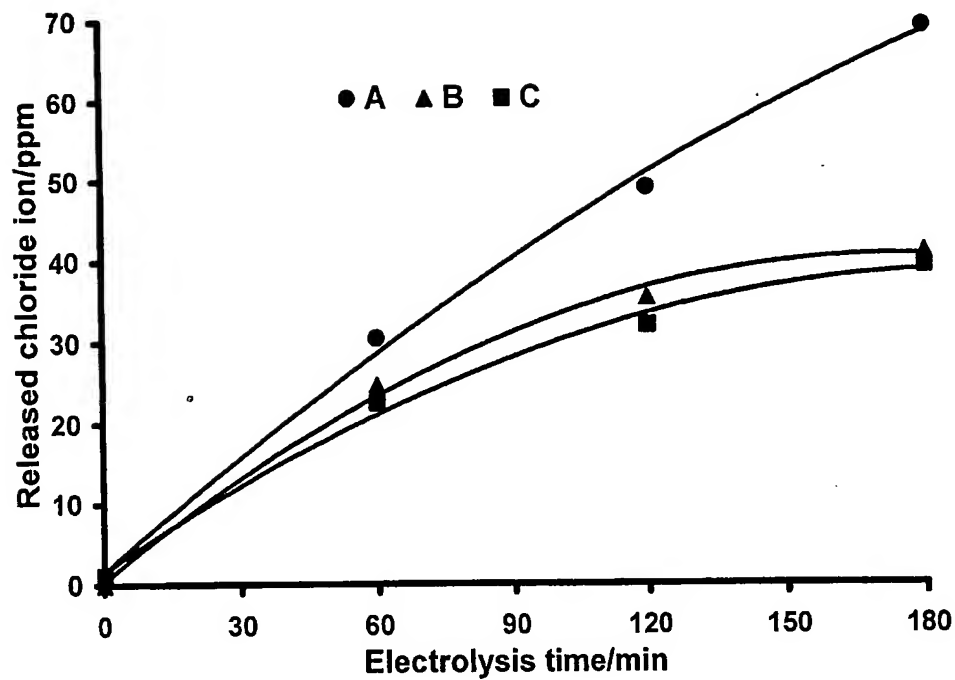


Figure 3

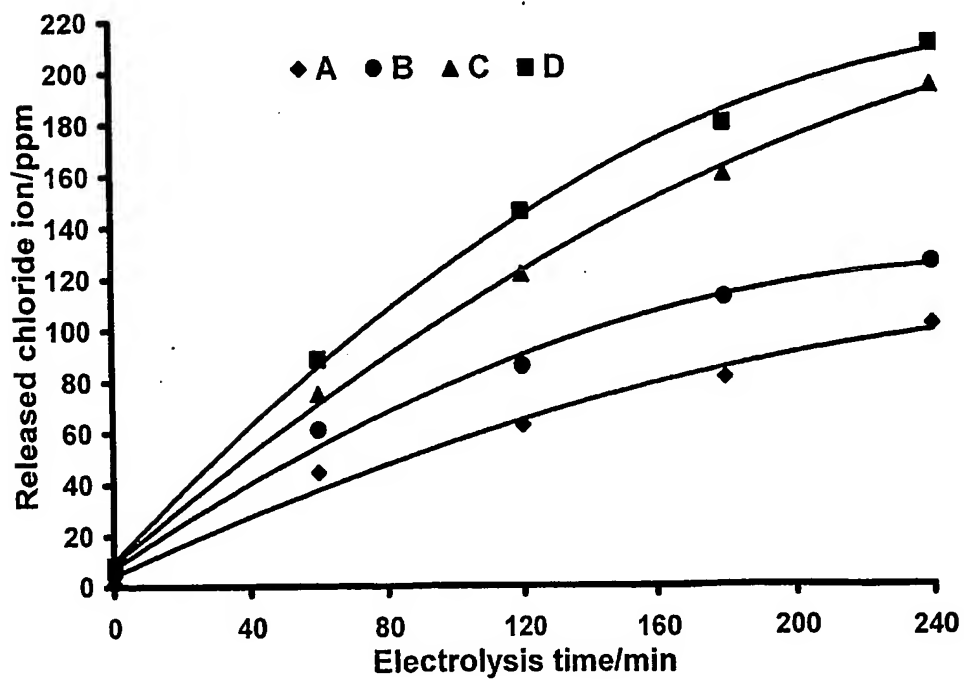


Figure 4

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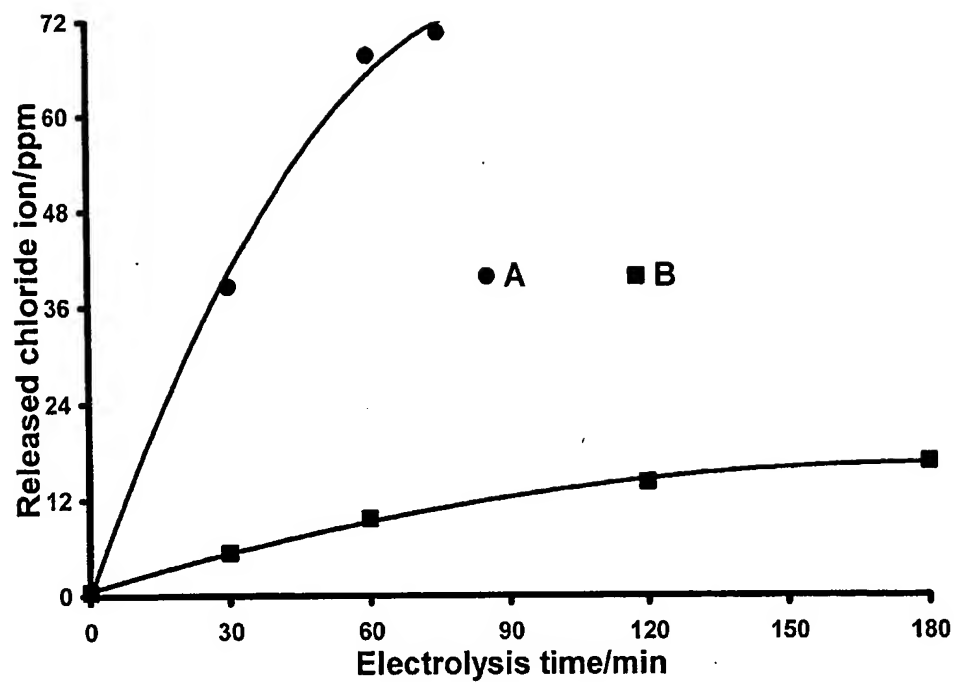


Figure 5

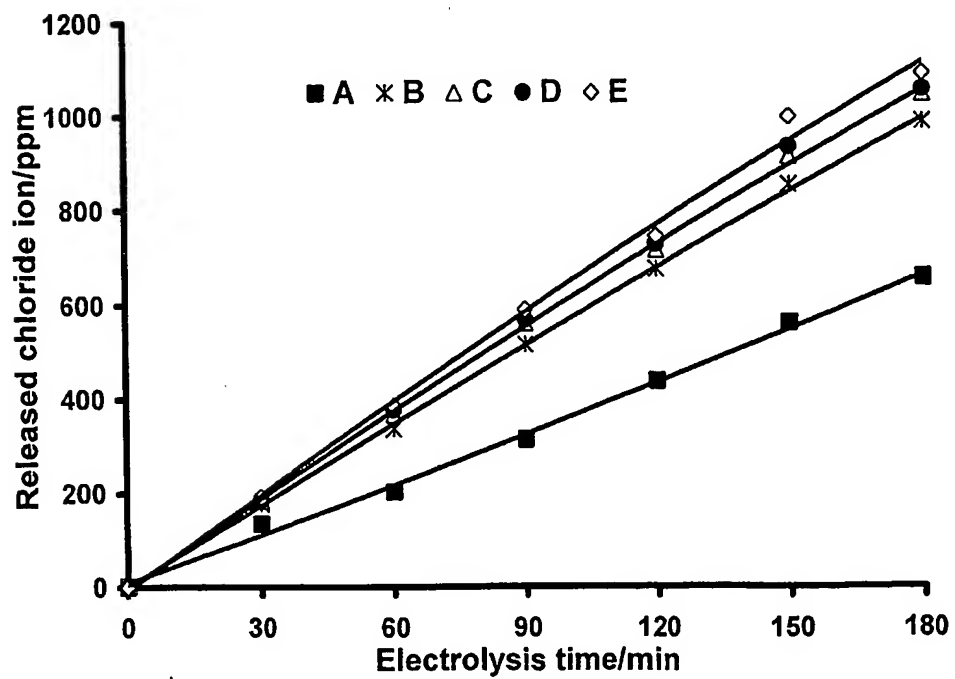


Figure 6

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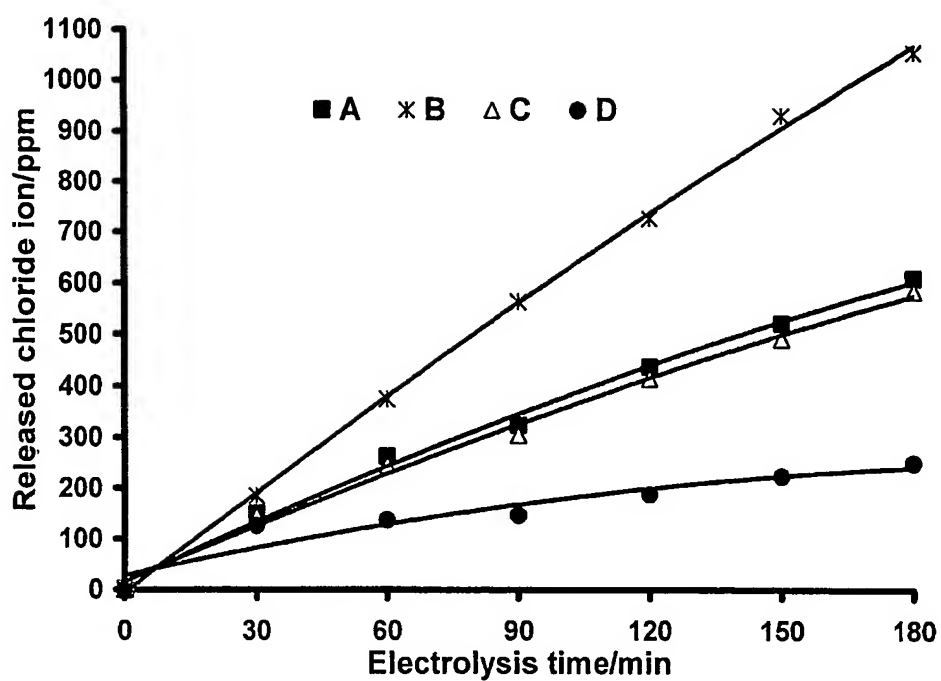


Figure 7

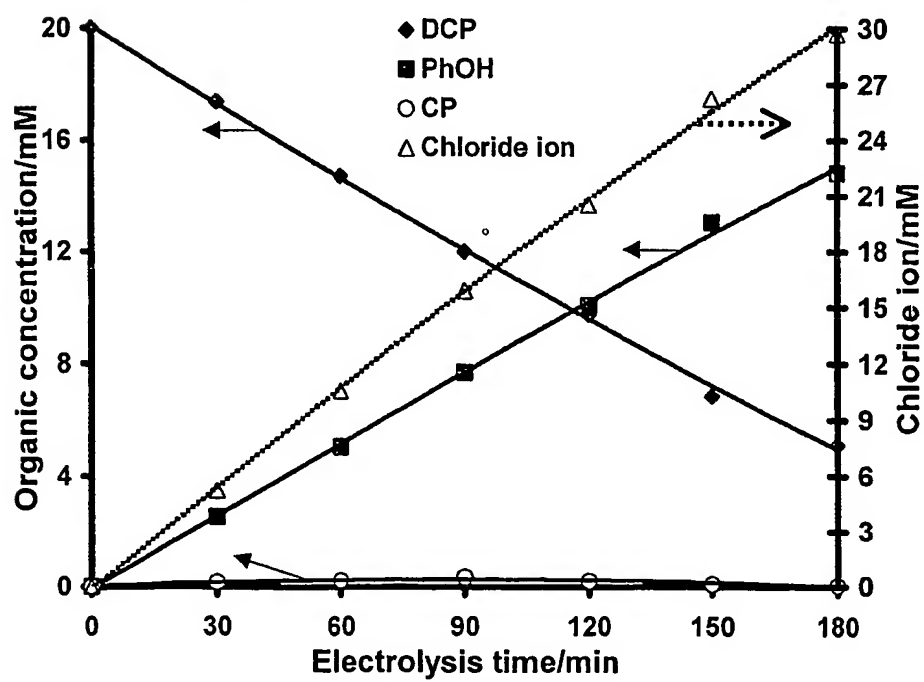


Figure 8

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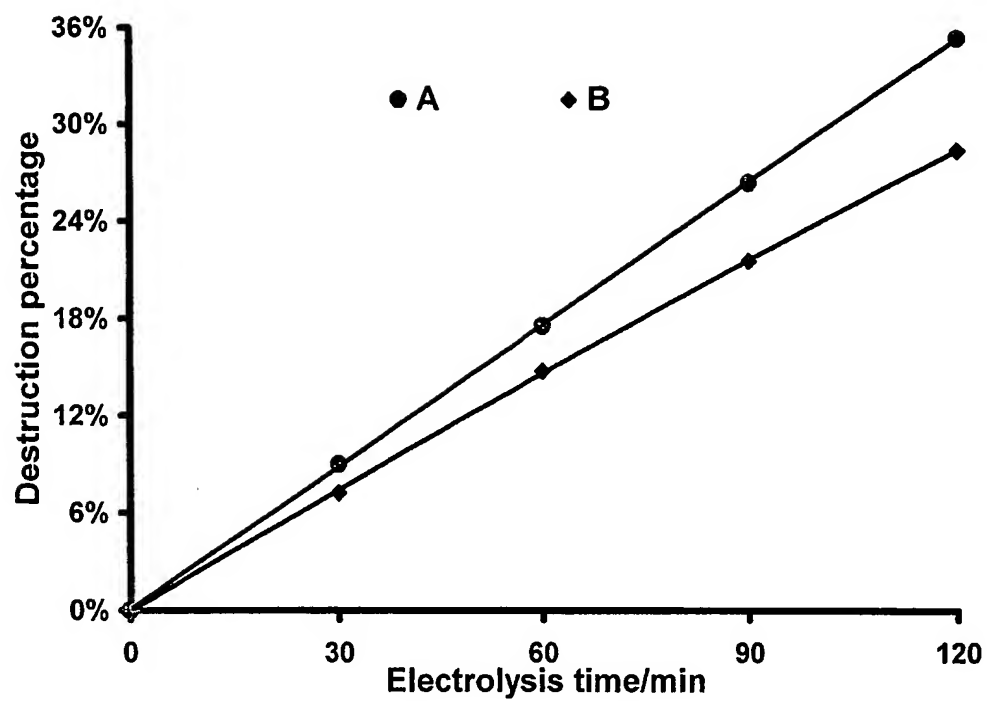


Figure 9